449. *Reactions of Unsaturated Compounds. Part XIV.* The Oxidation of* 2 : 2 : 4 : 6 : 6-*Pentamethylhept*-3-*ene.*

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2 : 2 : 4 : 6 : 6-Pentamethylhept-3-ene is oxidised by chromic acid in aqueous sulphuric acid to 2-*tert.*-butyl-2 : 4 : 4-trimethylpentanoic acid together with the normal products of oxidative fission. 2 : 2 : 4-Trimethylhex-1-ene and 2 : 2-dimethyl-4-ethylhex-3-ene similarly give tertiary carboxylic acids by oxidative rearrangement, although in relatively low yield.

The significance of these results is discussed in the light of other observations.

It has been shown[1,2] that the products of the oxidation of an olefin by chromic acid in aqueous sulphuric acid can be predicted qualitatively from a knowledge of the behaviour of the epoxide towards aqueous sulphuric acid. Striking examples of this are the formation of *tert.*-butyl methyl ketone (II*a*) from 2 : 3-dimethylbut-2-ene[1] (I*a*), of 2 : 2 : 3 : 3-tetramethylbutanoic acid (III*a*) from 2 : 2 : 4-trimethylpent-2-ene[3] (I*b*), and of 2 : 2 : 3-trimethylbutanoic acid (III*b*) from 2 : 4-dimethylpent-2-ene[2] (I*c*).

$RR'C{:}CR''R'''$ (I) $RR'R''C{\cdot}COR'''$ (II) $RR''R'''C{\cdot}CO_2H$ (III)

	R	R'	R''	R'''		R	R''	R'''
I*a* and II*a*	Me	Me	Me	Me	III*a*	Bu^t	Me	Me
I*b*	Bu^t	H	Me	Me	III*b*	Pr^i	Me	Me
I*c*	Pr^i	H	Me	Me	III*c*	Bu^t	Me	Et
I*d*	Bu^t	H	Me	Et	III*d*	Bu^t	Et	Et
I*e*	Bu^t	H	Et	Et	III*e*	Bu^t	Me	CH_2Bu^t
I*f*	Bu^t	H	Me	CH_2Bu^t				

This paper records the results of an extension of the examination to three trisubstituted olefins (I*d*, *e*, and *f*) to test the view that oxidation by chromic acid is dependent on the intermediate formation of an epoxide or its conjugate acid.

Oxidation of 2 : 2 : 4 : 6 : 6-pentamethylhept-3-ene (I*f*) by chromic acid in aqueous sulphuric acid gives a good yield of a tertiary carboxylic acid (III*e*) together with 2 : 2-dimethylpropanoic acid and methyl *neo*pentyl ketone, the normal products of oxidative fission. There is also formed a carbonyl compound having constants very close to those reported by Miner[4] for a compound isolated on oxidation of technical tri*iso*butylene, a mixture mainly of 2 : 2 : 4 : 6 : 6-pentamethylhept-3-ene and 4 : 4-dimethyl-2-*neo*pentylpent-1-ene. It is probable that Miner's carbonyl compound and ours are identical and this view is supported by the close agreement between the melting point of the oximes and 2 : 4-dinitrophenylhydrazones. Miner considered his compound to be 2 : 2 : 4 : 6 : 6-pentamethylheptane-3 : 5-dione. The substance we obtained has none of the properties of a 1 : 3-diketone and we suggest that it is 4-hydroxy-2 : 2 : 4 : 6 : 6-pentamethylheptan-3-one. The formation of such a compound is not unexpected and is in keeping with observations in the steroid series (cf. Fieser[5]).

The oxidation of 2 : 2 : 4-trimethylhex-3-ene (I*d*) and of 4-ethyl-2 : 2-dimethylhex-3-ene (I*e*) by chromic acid in aqueous sulphuric acid also gives the tertiary carboxylic acids (III*d*) and (III*c*) respectively, although in much lower yield than in the case of 2 : 2 : 4 : 6 : 6-pentamethylhept-3-ene. The main products are 2 : 2-dimethylpropanoic acid and ketones derived by oxidative fission. The neutral products of the oxidation of each olefin are

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* Part XIII, *J.*, 1957, 4195.

[1] Hickinbottom, Hogg, Peters, and Wood, *J.*, 1954, 4400.

[2] Hickinbottom, Peters, and Wood, *J.*, 1955, 1360.

[3] Byers and Hickinbottom, *J.*, 1948, 1334.

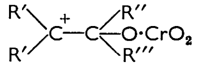
[4] Miner, Ph.D. Thesis, Penn. State College, Univ. Microfilms no. 260.

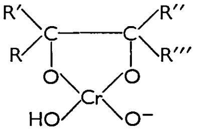
[5] Fieser, *J. Amer. Chem. Soc.*, 1953, **75**, 4386.

however more complex than can be accounted for on the basis of normal oxidative fission. Thus, from 2 : 2 : 4-trimethylhex-3-ene (I*d*) 3 : 5 : 5-trimethylhexan-2-one is obtained together with 2 : 2-dimethylpentan-2-one which is formed after isomerisation of the olefin to 2 : 2 : 4-trimethylhex-2-ene. Oxidation of these three olefins by chromic oxide in acetic anhydride was examined to determine if they give epoxides under these conditions. A relatively low yield of epoxide is obtained from 2 : 2 : 4 : 6 : 6-pentamethylhept-3-ene (I*f*). 4-Ethyl-2 : 2-dimethylhex-3-ene (I*e*) gave an even smaller yield; none could be detected in the products of oxidation of 2 : 2 : 4-trimethylhex-3-ene (I*d*).

It is known from previous work [2,6] that the isolation of epoxides from chromic oxide–acetic anhydride oxidations is dependent on a number of factors, resistance to further oxidation and to ring opening being the most important. The above results could therefore be adequately accounted for on the basis of sensitivity of the epoxide were it not for the discrepancy between the relatively high yield of 2-*tert.*-butyl-2 : 4 : 4-trimethylpentanoic acid (III*e*) from 2 : 2 : 4 : 6 : 6-pentamethylhept-3-ene (I*f*) in aqueous chromic acid–sulphuric acid and the poor yield of the aldehyde corresponding to (III*e*) when the epoxide is treated with aqueous sulphuric acid. These observations reinforce the earlier conclusions that the epoxide is not the true intermediate in any of the chromic acid oxidations. Conclusive evidence for this view is provided by observations on some 1 : 1-diaryl-2-methylpropenes;[6] these give epoxides in high yield by reaction with chromic oxide in acetic anhydride, yet are oxidised by aqueous sulphuric–chromic acid faster than the epoxide is hydrated by aqueous sulphuric acid of the same strength.

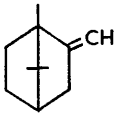
(IV)





(V)

It is these observations which have confirmed the view that the epoxide is not the true intermediate in the oxidation, but that in suitable circumstances it can be derived from some addition complex of the olefin and the oxidising agent. In an earlier paper, it was suggested that electrophilic addition of chromic oxide would give a complex of the type (IV), and that all the known ways in which oxidation at the double bond can occur may be adequately represented in terms of such an addition complex.[2] In this formulation (IV) the $O{\cdot}CrO_2$ addendum is representational of any form of oxygenated Cr^{VI} grouping. The possible development of a negative charge on the addendum is ignored.



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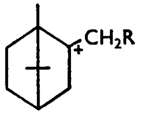

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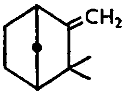
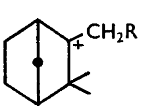


(VIII)



(IX)

Zeiss and Zwanzig [7] have suggested an alternative formulation (V) for the initial phase of the reaction between the olefin and chromic acid. They base their choice on the assumption that if (IV) represented the first stage rearrangement should occur in the cyclic system of 1-methyl-α-fenchene (VI); this is not observed when the oxidation is carried out by chromic acid in acetic acid solution. They have argued that because the system (VII; R = H) is prone to rearrangement, the system (VII) when R = OH or $O{\cdot}CrO_2$ should rearrange in the same way. That this argument is not sound can be shown by reference to camphene (VIII). This has been examined in much greater detail than 1-methyl-α-fenchene, and its derived system (IX; R = H) is known to be sensitive to

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[6] Hickinbottom and Moussa, *J.*, 1957, 4195.

[7] Zeiss and Zwanzig, *Chem. and Ind.*, 1956, 545.

rearrangement to bornyl derivatives. On the other hand, camphene oxide isomerises to camphenilanaldehyde on treatment with aqueous mineral acid with no recognisable alteration in the ring system.[8] It is reasonably certain that this change occurs through the carbonium ion (IX; R = OH) which is comparable in form with the addition complex (IX; R = O·CrO_2) which we postulated for the initial stage of the oxidation. Further, when camphene is oxidised by chromic oxide in acetic anhydride, camphene oxide is formed; [8] under more drastic conditions, camphenilone and camphenilanic acid are formed without any recognisable alteration in the ring system.[9] Zeiss and Zwanzig's formulation has other disadvantages: it does not explain the oxidative rearrangements which are characteristic of some olefins, such as 2 : 2 : 4 : 6 : 6-pentamethylhept-3-ene, 2 : 2 : 4-trimethylpent-2-ene, or 2 : 4-dimethylpent-2-ene; nor would it have been possible to predict from it the formation of epoxides from olefins by oxidation in anhydrous solvents. A more serious objection lies in its failure to account for the formation of 1 : 4-diketones [10] when some steroidal conjugated dienes are oxidised by dichromate in acetic acid: indeed it prohibits the formation of 1 : 4-diketones. The formal resemblance between the electrophilic addition of halogen or halogen hydrides to conjugated dienes and the results of the oxidation of these dienes by chromic acid is sufficiently striking to make the form of addition of chromic oxide that we have suggested seem more than probable.

EXPERIMENTAL

Oxidation of 2 : 2 : 4 : 6 : 6-*Pentamethylhept*-3-*ene*.—(a) *By aqueous sulphuric and chromic acid.* The olefin [11] (50 g.) was added in small portions to a stirred mixture of sodium dichromate (180 g.) and aqueous sulphuric acid (60% w/v; 900 c.c.), each portion being allowed to react completely before further addition was made. About 12 hr. were required to complete the addition and the temperature was kept between 30° and 40°. Stirring was continued for 4 hr. after all the olefin had been added; the mixture was then diluted with water (2 l.) and extracted with ether. The acid products, removed from the combined ether extracts by alkali, were separated by distillation into 2 : 2-dimethylpropanoic acid (7·5 g.) (*p*-toluidide, m. p. and mixed m. p. 120°) and 2-*tert.*-butyl-2 : 4 : 4-trimethylpentanoic acid (17·5 g.), m. p. 130° (from acetone) (Found: C, 72·5; H, 12·3%; equiv., 196. Calc. for $C_{12}H_{24}O_2$: C, 72·0; H, 12·1%; equiv., 200). The absence of an appreciable amount of di*neo*pentylacetic acid in the product was demonstrated by treatment successively with thionyl chloride and aqueous ammonia; no amide was formed. Under these conditions di*neo*pentylacetic acid gives an amide; 2-*tert.*-butyl-2 : 4 : 4-trimethylpentanoic acid gives only the free acid (cf. Conant and Wheland [12]). Hence it may be concluded that there is no isomerisation of the olefin during its oxidation.

The butyltrimethylpentanoic acid in concentrated sulphuric acid at 180—200° behaves as a tertiary carboxylic acid, the carboxyl group being eliminated as carbon monoxide (80% yield) during 15 min.

Attempts to reduce the acid by lithium aluminium hydride in boiling ether failed. Reduction of the acid chloride (b. p. 101°/11 mm., n_D^{20} 1·4646; from the acid and boiling thionyl chloride) gave an alcohol which was not characterised except by oxidising it with *tert.*-butyl chromate to 2-*tert.*-butyl-2 : 4 : 4-trimethylpentanal (2 : 4-dinitrophenylhydrazone, needles, m. p. 152—153° not depressed on admixture with a specimen prepared from 3 : 4-epoxy-2 : 2 : 4 : 6 : 6-pentamethylheptane [11]).

The neutral products of the oxidation were resolved by distillation into 4 : 4-dimethylpentan-2-one (b. p. 26—35°/14 mm., n_D^{20} 1·4050—1·4061, 1·5 g.; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 100—101°) and material of b. p. 80—92°/14 mm., n_D^{20} 1·4310—1·4352 (7·6 g.). The latter material was not homogeneous, but contained a ketone which was characterised by its 2 : 4-dinitrophenylhydrazone {needles, m. p. 134°, after chromatographing on

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[8] Hickinbottom and Wood, *J.*, 1953, 1906.

[9] Treibs and Schmidt, *Ber.*, 1928, **61**, 464.

[10] Fieser *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 2397; 1953, **75**, 116, 121; Elks, Evans, Long, and Thomas, *J.*, 1954, 452; Budziarek, Newbold, Stevenson, and Spring, *J.*, 1952, 2892; Barton and Laws, *J.*, 1954, 52.

[11] Davis and Hickinbottom, *J.*, 1957, 1998.

[12] Conant and Wheland, *J. Amer. Chem. Soc.*, 1933, **55**, 2502.

alumina [benzene–light petroleum (b. p. 60—80°)] (Found: C, 56·7; H, 6·9; N, 15·4. Calc. for $C_{18}H_{28}O_5N_4$: C, 56·8; H, 7·4; N, 14·7. Calc. for $C_{18}H_{26}O_5N_4$: C, 57·1; H, 6·9; N, 14·8%)}. An oxime, prepared in refluxing pyridine, had m. p. 128—129° (from alcohol). No crystalline semicarbazone could be isolated from the crude carbonyl compound. Miner's carbonyl compound [4] had b. p. 89°/16 mm., n_D^{20} 1·4320, and gave a 2 : 4-dinitrophenylhydrazone, m. p. 133—134°, oxime, m. p. 129—130°, and semicarbazone, m. p. 127—128°.

(b) *By chromic oxide in acetic anhydride.* An ice-cold solution of dried chromic oxide (15 g.) in acetic anhydride (15 c.c.) diluted with carbon disulphide (100 c.c.) was prepared by cautious addition of the chromic oxide–acetic anhydride in 1 c.c. portions to 10 c.c. of carbon disulphide. It is important to keep the reagents at 0° or below during this stage and subsequently, otherwise violent decomposition may occur.

This reagent was added in 1 c.c. portions to the olefin (46 g.) in carbon disulphide (100 c.c.), at −12°, and stirred during the addition and for 3½ hr. afterwards. A heavy dark precipitate was collected, and the filtrate shaken with sodium carbonate solution till neutral, then dried and distilled.

A considerable amount of unchanged olefin, b. p. 60°/12 mm., n_D^{20} 1·4340—1·4385, was obtained. It was followed by a fraction, b. p. 77—84°/12 mm., n_D^{20} 1·4443 (1·6 g.), which was not homogeneous; the presence of epoxide was demonstrated by the formation of the 2 : 4-dinitrophenylhydrazone of 2-*tert.*-butyl-2 : 4 : 4-trimethylpentanal (m. p. and mixed m. p. 152—153°) when it was warmed with aqueous-alcoholic 30% sulphuric acid containing 2 : 4-dinitrophenylhydrazine.

The higher-boiling fractions of the product (4 g.), b. p. 84°/11 mm., n_D^{20} 1·4480, did not give a pure compound.

The forerunnings of the distillation and the contents of the cold trap (1 g.) contained some methyl *neo*pentyl ketone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 100°).

Oxidation of 2 : 2 : 4-*Trimethylhex*-3-*ene by Aqueous Sulphuric and Chromic Acid.*—The olefin [13] (75 g.) was added to a solution of chromic oxide (270 g.) in aqueous sulphuric acid (60% w/v; 100 c.c.) at 20—30°, as described above for 2 : 2 : 4 : 6 : 6-pentamethylhept-3-ene. The acidic products of the oxidation were 2 : 2-dimethylpropanoic acid (12 g.) and 2-*ethyl*-2 : 3 : 3-*trimethylbutanoic acid* (4·4 g.), b. p. 122—130°/22 mm., m. p. 103—104° (from aqueous alcohol) (Found: C, 68·4; H, 11·4%; equiv., 151. $C_9H_{18}O_2$ requires C, 68·3; H, 11·5%; equiv., 158). This acid gave 75% of the theoretical amount of carbon monoxide when it was heated for ½ hr. with concentrated sulphuric acid at 180—200°.

The neutral products were ethyl methyl ketone (b. p. 70—74°: 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 110—111°) and methyl *neo*pentyl ketone, identified as above. The conditions of the oxidation were varied by adding the oxidising agent [chromic oxide (30 g.) in water (300 c.c.)] to a stirred suspension of the olefin (25 g.) in 70% w/v sulphuric acid (250 c.c.). The acidic products were 2 : 2-dimethylpropanoic acid (1·1 g.) and 2-ethyl-2 : 3 : 3-trimethylbutanoic acid (0·8 g.). From the neutral portion of the product, there were isolated, ethyl methyl ketone (0·5 g.), methyl *neo*pentyl ketone (2·2 g.), and 3 : 5 : 5-trimethylhex-2-one (8 g.), b. p. 80—83°/63 mm., n_D^{20} 1·4190—1·4200 (2 : 4-dinitrophenylhydrazone, m. p. 56—59°, raised to 59—61° on admixture with an authentic specimen).

Oxidation of 4-*Ethyl*-2 : 2-*dimethylhex*-3-*ene.*—(a) *By aqueous sulphuric and chromic acid.* The olefin (70 g.) was added to a stirred solution of sodium dichromate (300 g.) in 60% w/v sulphuric acid (1400 c.c.) at 30—40° during 20 hr. The acid products were resolved by distillation into 2 : 2-dimethylpropanoic acid (20 g., crude) and a semisolid acid, b. p. 130—132°/12 mm. (3·5 g.), which was purified with some loss from aqueous acetone: the pure *acid* melted at 67° (Found: C, 69·7; H, 11·6%; equiv., 167. $C_{10}H_{20}O_2$ requires C, 69·7; H, 11·7%; equiv., 172), and had the characteristics of a tertiary acid; in concentrated sulphuric at 200° 87% of the theoretical amount of carbon monoxide was evolved.

From the neutral products diethyl ketone was isolated (3·8 g.) (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 154°). A second ketone was present in the fraction, b. p. 43—53°/11 mm. (1·4 g.); it was characterised by its 2 : 4-dinitrophenylhydrazone, leaflets [from ethyl acetate–light petroleum (b. p. 60—80°)], m. p. 133—134°, depressed on admixture with 5 : 5-dimethylhexan-3-one 2 : 4-dinitrophenylhydrazone, m. p. 135°.

(b) *By chromic oxide in acetic anhydride.* A solution of chromic oxide (16 g.) in acetic anhydride (16 c.c.) diluted with carbon disulphide (100 c.c.) was added in 1 c.c. portions to

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[13] Whitmore *et al.*, *J. Amer. Chem. Soc.*, 1941, **63**, 643.

4-ethyl-2 : 2-dimethylhex-3-ene (56 g.) in carbon disulphide. The products were diethyl ketone (5 g.) (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 154°) and fractions, b. p. 46—68°/17 mm., n_D^{20} 1·4280—1·4290 (9 g.), which could not be efficiently resolved by distillation. By shaking them with aqueous sulphuric acid (0·5%) for 24 hr. and then removing volatile matter, a viscous residue was left having the characteristics of a glycol. It gave, on oxidation by periodic acid, 2 : 2-dimethylpropanal (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 210°) and diethyl ketone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 154°). A considerable amount of unchanged olefin was recovered, having b. p. 36—46°/17 mm., n_D^{20} 1·4300—1·4291.

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